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SUPPORTING INFORMATION

Copper-Catalyzed Asymmetric Ring Opening of Oxabicyclic Alkenes with Organolithium Reagents

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General procedure for the copper-catalyzed asymmetric ring opening of oxabicyclic alkenes	S4
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General Procedures:

Chromatography: Merck silica gel type 9385 230-400 mesh, TLC: Merck silica gel 60, 0.25 mm. Components were visualized by UV and cerium/molybdenum or potassium permanganate staining. Progress and conversion of the reaction were determined by GC-MS (GC, HP6890; MS HP5973) with an HP1 or HP5 column (Agilent Technologies, Palo Alto, CA). Mass spectra were recorded on an AEI-MS-902 mass spectrometer (EI+) or a LTQ Orbitrap XL (ESI+). ^1H - and ^{13}C -NMR were recorded on a Varian AMX400 (400 and 100.59 MHz, respectively) or a Varian VXR300 (300 and 75 MHz, respectively) using CDCl_3 as solvent. Chemical shift values are reported in ppm with the solvent resonance as the internal standard (CHCl_3 : δ 7.26 for ^1H , δ 77.0 for ^{13}C). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. Optical rotations were measured on a *Schmidt + Haensch* polarimeter (Polartronic MH8) with a 10 cm cell (c given in g/100 mL). Enantiomeric excesses were determined by HPLC analysis using a Shimadzu LC-10ADVP HPLC equipped with a Shimadzu SPD-M10A VP diode array detector.

All reactions were carried out under a nitrogen atmosphere using oven dried glassware and using standard Schlenk techniques. Dichloromethane was dried and distilled over calcium hydride; 1,2-dichloroethane was dried over molecular sieves (3Å). $\text{CuBr}\cdot\text{SMe}_2$ was purchased from Aldrich, and used without further purification. Organolithium reagents **2** were purchased from Acros: n -BuLi (**2a**) (1.6 M in hexane), i -BuLi (**2d**) (1.6 M in hexane), TMSCH_2Li (**2e**) (0.8 M in hexane), MeLi (**2f**) (1.6 M in diethyl ether) or Aldrich: EtLi (**2b**) (0.5 M in benzene/cyclohexane 9:1), n -HexLi (**2c**) (2.3 M in n -hexane), PhLi (**2g**) (1.8 M in dibutyl ether). Ligand **L1** was purchased from Aldrich. Phosphoramidite ligands **L2**, **L4**¹ and **L3**, **L5**² were prepared as reported in the literature.

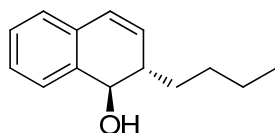
Racemic products were synthesized by reaction of the oxabicyclic alkenes **1** with the corresponding organolithium reagent **2** at -80°C in dichloromethane in the presence of CuI (10 mol%) and PPh_3 (20 mol%).

¹ Feringa, B. L.; Pineschi, M.; Arnold, L. A.; Imbos, R.; De Vries, A. H. M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2620–2623.

² Tissot-Croset, K.; Polet, D.; Gille, S.; Hawner, C.; Alexakis, A. *Synthesis* **2004**, 2586–2590.

General procedure for the copper-catalyzed ring opening of oxabicyclic alkenes **1** with organolithium reagents **2**

A Schlenk tube equipped with septum and stirring bar was charged with CuBr•SMe₂ (0.01 mmol, 2.06 mg, 5 mol%) and phosphoramidite ligand (*R,R,R*)-**L2** (0.012 mmol, 6.48 mg, 6 mol%). Dry dichloromethane (2 mL) was added and the solution was stirred under nitrogen at room temperature for 15 min. Then, oxabicyclic alkene **1** (0.2 mmol) was added and the resulting solution was cooled to -80 °C. To the cooled mixture, BF₃•OEt₂ (28 μL, 0.22 mmol, 1.1 eq) was added with a microsyringe. In a separate Schlenk vessel, the corresponding organolithium reagent **2** (0.22 mmol, 1.1 eq) was diluted with dry hexane (combined volume of 1 mL) under nitrogen and added dropwise to the reaction mixture over 2 hours using a syringe pump. Once the addition was complete, the mixture was stirred overnight at -80°C. The reaction was quenched with a saturated aqueous NH₄Cl solution (2 mL) and the mixture was warmed up to room temperature, diluted with diethyl ether and the layers were separated. The aqueous layer was extracted with diethyl ether (3 x 5 mL) and the combined organic layers were dried with anhydrous Na₂SO₄, filtered and the solvent was evaporated *in vacuo*. The crude product was purified by flash chromatography on silica gel using a gradient of *n*-pentane:Et₂O (15:1 – 9:1) as the eluent.



(+)-(1*R*,2*S*)-2-butyl-1,2-dihydronaphthalen-1-ol (3aa): Isolated as a white solid.

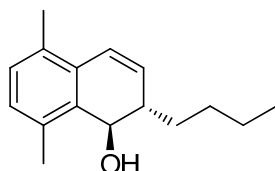
[84% yield, >99:1 anti:syn, 97% ee].

The physical data were identical in all respects to those previously reported.³

[α]_D²⁰ = +230.0 (*c* = 1.0, CHCl₃), [lit.³ (-)-(1*S*,2*R*)-**3aa** (92% ee): [α]_D²⁰ = -233.0 (*c* = 0.94, CHCl₃)].

Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel OD-H column, 0.5 mL/min, *n*-heptane/*i*-PrOH 98:2, 40 °C, 254 nm, retention times (min.): 23.1 (minor) and 26.5 (major).

³ Bertozzi, F.; Pineschi, M.; Macchia, F.; Arnold, L. A.; Minnaard, A. J.; Feringa, B. L. *Org. Lett.* **2002**, *4*, 2703-2705.



(+)-2-butyl-5,8-dimethyl-1,2-dihydronaphthalen-1-ol (3ba): Isolated as a pale yellow oil.

[82% yield, >99:1 anti:syn, 95% ee].

^1H NMR: (400 MHz, CDCl_3) δ 7.00 (q, $J = 7.7$ Hz, 2H), 6.71 (d, $J = 9.9$ Hz, 1H), 6.11 (dd, $J = 9.8, 5.9$ Hz, 1H), 4.76 (s, 1H), 2.63 (dd, $J = 13.8, 6.7$ Hz, 1H), 2.40 (s, 3H), 2.33 (s, 3H), 1.70 (bs, 1H), 1.43 – 1.10 (m, 6H), 0.87 (t, $J = 7.1$ Hz, 3H).

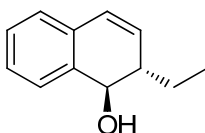
^{13}C NMR: (100 MHz, CDCl_3) δ 134.3, 132.7, 131.5, 130.4, 130.0, 129.9, 129.4, 122.6, 68.1, 42.1, 31.6, 29.9, 22.8, 18.9, 18.2, 14.0.

$[\alpha]_{\text{D}}^{20} = +357.0$ ($c = 1.0$, CHCl_3).

HRMS (ESI+, m/z): calcd for $\text{C}_{16}\text{H}_{23}\text{O}$ $[\text{M}+\text{H}]^+$: 231.17434; found: 231.17329.

Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel OD-H column, 0.5 mL/min, *n*-heptane/*i*-PrOH 99:1, 40 °C, 254 nm, retention times (min): 24.3 (minor) and 27.1 (major).

In accordance with the results obtained in the other ring opening reactions, the absolute configuration of this compound is assumed to be (1*R*, 2*S*), analogous to the other products.



(+)-(1*R*,2*S*)-2-ethyl-1,2-dihydronaphthalen-1-ol (3ab): Isolated as a white solid

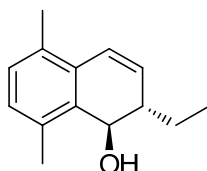
[80% yield, >99:1 anti:syn, 98% ee].

The physical data were identical in all respects to those previously reported.^{3,4}

$[\alpha]_{\text{D}}^{20} = +245.0$ ($c = 1.0$, CHCl_3).

Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel OD-H column, 0.5 mL/min, *n*-heptane/*i*-PrOH 99:1, 40 °C, 254 nm, retention times (min.): 44.9 (minor) and 51.9 (major).

⁴ Bertozzi, F.; Crotti, P.; Del Moro, F.; Feringa, B. L.; Macchia, F.; Pineschi, M. *Chem. Commun.* **2001**, 2606-2607.

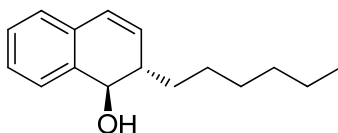


(+)-(1*R*,2*S*)-2-ethyl-5,8-dimethyl-1,2-dihydronaphthalen-1-ol (3bb): Isolated as a pale yellow oil. [71% yield, >99:1 anti:syn, 97% ee].

The physical data were identical in all respects to those previously reported.³

$[\alpha]_{\text{D}}^{20} = +250.6$ ($c = 0.53$, CHCl_3), [lit.³ (-)-(1*S*,2*R*)-**3bb** (99% ee): $[\alpha]_{\text{D}}^{20} = -256.16$ ($c = 2.66$, CHCl_3)].

Enantiomeric excess was determined by chiral HPLC analysis, Chiralpak AD column, 1.0 mL/min, *n*-heptane/*i*-PrOH 99:1, 40 °C, 254 nm, retention times (min.): 14.2 (minor) and 15.8 (major).



(+)-2-hexyl-1,2-dihydronaphthalen-1-ol (3ac): Isolated as a white solid.

[81% yield, >99:1 anti:syn, 97% ee].

¹H NMR: (400 MHz, CDCl_3) δ 7.36 (dd, $J = 7.2, 0.8$ Hz, 1H), 7.25 (dq, $J = 14.4, 7.4, 1.5$ Hz, 2H), 7.11 (dd, $J = 7.2, 1.2$ Hz, 1H), 6.49 (d, $J = 9.7$ Hz, 1H), 6.02 (dd, $J = 9.6, 4.8$ Hz, 1H), 4.52 (s, 1H), 2.70 – 2.45 (m, 1H), 1.79 (d, $J = 5.2$ Hz, 1H), 1.48 – 1.34 (m, 2H), 1.34 – 1.19 (m, 8H), 0.87 (t, $J = 6.8$ Hz, 3H).

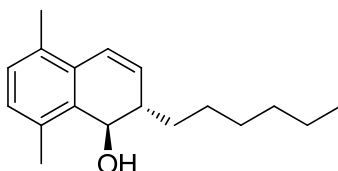
¹³C NMR: (100 MHz, CDCl_3) δ 135.7, 132.3, 131.1, 128.5, 127.8, 127.6, 126.4, 125.8, 72.4, 42.5, 31.7, 31.6, 29.4, 27.0, 22.6, 14.0.

$[\alpha]_{\text{D}}^{20} = +311.1$ ($c = 1.0$, CHCl_3).

HRMS (ESI+, m/z): calcd for $\text{C}_{16}\text{H}_{22}\text{ONa}$ $[\text{M}+\text{Na}]^+$: 253.15798; found: 253.15647.

Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel OD-H column, 0.5 mL/min, *n*-heptane/*i*-PrOH 99:1, 40 °C, 254 nm, retention times (min): 33.0 (minor) and 39.9 (major).

In accordance with the results obtained in the other ring opening reactions, the absolute configuration of this compound is assumed to be (1*R*, 2*S*), analogous to the other products.



(+)-2-hexyl-5,8-dimethyl-1,2-dihydronaphthalen-1-ol (3bc): Isolated as a pale yellow oil. [82% yield, >99:1 anti:syn, 93% ee].

^1H NMR: (400 MHz, CDCl_3) δ 7.00 (q, $J = 7.7$ Hz, 2H), 6.71 (d, $J = 9.9$ Hz, 1H), 6.10 (dd, $J = 9.8, 5.9$ Hz, 1H), 4.76 (s, 1H), 2.63 (dd, $J = 13.3, 6.5$ Hz, 1H), 2.40 (s, 3H), 2.33 (s, 3H), 1.72 (s, 1H), 1.48 – 1.32 (m, 2H), 1.32 – 1.12 (m, 8H), 0.87 (t, $J = 6.7$ Hz, 3H).

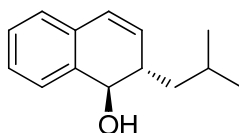
^{13}C NMR: (100 MHz, CDCl_3) δ 134.3, 132.7, 131.5, 130.4, 130.0, 129.9, 129.4, 122.5, 68.1, 42.1, 31.8, 31.7, 29.4, 27.6, 22.6, 18.9, 18.2, 14.0.

$[\alpha]_{\text{D}}^{20} = +272.8$ ($c = 1.0$, CHCl_3).

HRMS (ESI+, m/z): calcd for $\text{C}_{18}\text{H}_{27}\text{O}$ $[\text{M}+\text{H}]^+$: 259.20564; found: 259.20575.

Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel OD-H column, 0.5 mL/min, *n*-heptane/*i*-PrOH 99:1, 40 °C, 254 nm, retention times (min): 20.7 (minor) and 23.6 (major).

In accordance with the results obtained in the other ring opening reactions, the absolute configuration of this compound is assumed to be (1*R*, 2*S*), analogous to the other products.



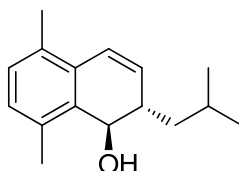
(+)-(1*R*,2*S*)-2-isobutyl-1,2-dihydronaphthalen-1-ol (3ad): Isolated as a white solid [86% yield, >99:1 anti:syn, 97% ee].

The physical data were identical in all respects to those previously reported.⁵

$[\alpha]_{\text{D}}^{20} = +270.6$ ($c = 1.0$, CHCl_3), [lit.⁵ (-)-(1*S*,2*R*)-**3ad** (94% ee): $[\alpha]_{\text{D}}^{20} = -345.9$ ($c = 0.66$, CHCl_3)].

Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel OD-H column, *n*-heptane/*i*-PrOH 98:2, 40 °C, 254 nm, retention times (min.): 22.2 (minor) and 25.7 (major).

⁵ Millet, R.; Gremaud, L.; Bernardez, T.; Palais, L.; Alexakis, A. *Synthesis* **2009**, 2101-2112.



(+)-2-isobutyl-5,8-dimethyl-1,2-dihydronaphthalen-1-ol (3bd): Isolated as a pale yellow oil. [96% yield, >99:1 anti:syn, 93% ee].

^1H NMR: (400 MHz, CDCl_3) δ 7.00 (q, $J = 7.7$ Hz, 2H), 6.71 (d, $J = 9.9$ Hz, 1H), 6.09 (dd, $J = 9.8, 6.0$ Hz, 1H), 4.72 (s, 1H), 2.74 (dd, $J = 14.6, 6.9$ Hz, 1H), 2.39 (s, 3H), 2.33 (s, 3H), 1.86 – 1.60 (m, 2H), 1.15 – 1.00 (m, 2H), 0.94 (d, $J = 6.6$ Hz, 3H), 0.89 (d, $J = 6.6$ Hz, 3H).

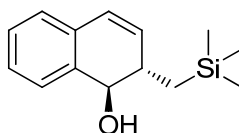
^{13}C NMR: (100 MHz, CDCl_3) δ 134.3, 132.6, 131.5, 130.4, 130.0, 129.9, 129.4, 122.6, 68.3, 40.8, 39.8, 25.8, 23.2, 22.3, 18.9, 18.2.

$[\alpha]_{\text{D}}^{20} = +345.0$ ($c = 1.0$, CHCl_3).

HRMS (ESI+, m/z): calcd for $\text{C}_{16}\text{H}_{23}\text{O}$ $[\text{M}+\text{H}]^+$: 231.17434; found: 231.17421.

Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel OD-H column, 0.5 mL/min, *n*-heptane/*i*-PrOH 99.5:0.5, 40 °C, 254 nm, retention times (min): 40.2 (major) and 43.1 (minor).

In accordance with the results obtained in the other ring opening reactions, the absolute configuration of this compound is assumed to be (1*R*, 2*S*), analogous to the other products.



(+)-2-((trimethylsilyl)methyl)-1,2-dihydronaphthalen-1-ol (3ae): Isolated as a white solid. [65% yield, >99:1 anti:syn, 43% ee].

^1H NMR: (400 MHz, CDCl_3) δ 7.34 (d, $J = 7.4$ Hz, 1H), 7.26 (dt, $J = 16.5, 7.3$ Hz, 2H), 7.12 (d, $J = 7.3$ Hz, 1H), 6.45 (d, $J = 9.6$ Hz, 1H), 6.02 (dd, $J = 9.6, 5.1$ Hz, 1H), 4.43 (s, 1H), 2.68 (td, $J = 9.8, 5.0$ Hz, 1H), 1.79 (s, 1H), 0.69 (dd, $J = 14.4, 5.1$ Hz, 1H), 0.50 (dd, $J = 14.4, 10.3$ Hz, 1H), 0.05 (s, 9H).

^{13}C NMR: (100 MHz, CDCl_3) δ 135.3, 132.7, 132.2, 128.6, 128.3, 127.6, 126.5, 125.0, 75.1, 38.9, 19.2, -0.6.

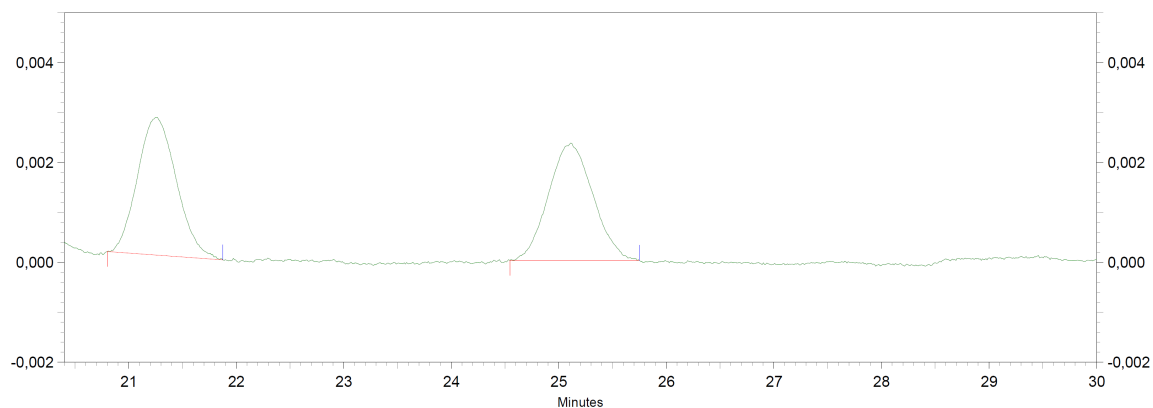
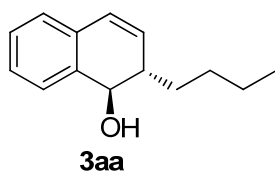
$[\alpha]_{\text{D}}^{20} = +84.7$ ($c = 1.0$, CHCl_3).

HRMS (ESI+, m/z): calcd for $\text{C}_{14}\text{H}_{21}\text{OSi}$ $[\text{M}+\text{H}]^+$: 233.13562; found: 233.13466.

Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel OD-H column, 0.5 mL/min, *n*-heptane/*i*-PrOH 98:2, 40 °C, 261 nm, retention times (min): 18.0 (minor) and 18.9 (major).

In accordance with the results obtained in the other ring opening reactions, the absolute configuration of this compound is assumed to be (1*R*, 2*S*), analogous to the other products.

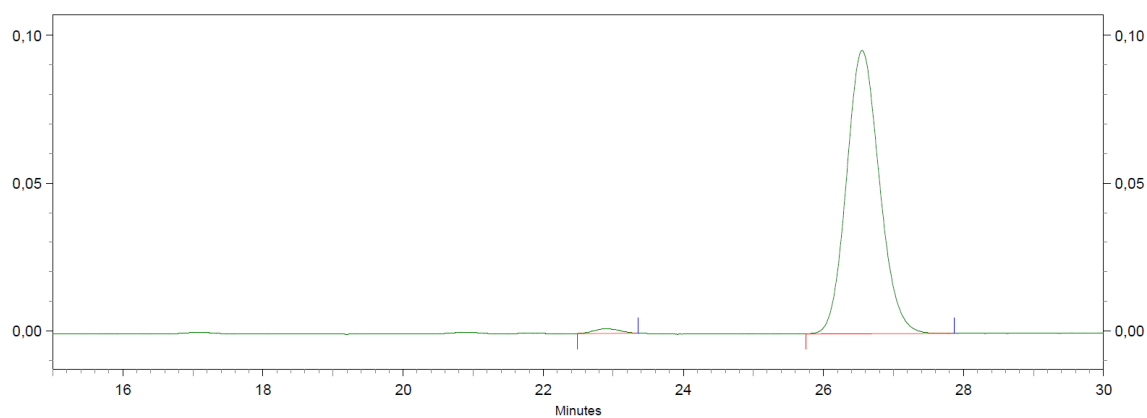
HPLC traces of ringopened products



1: 265 nm, 8 nm Results

Pk #	Name	Retention Time	Area	Area Percent
1	Peak @ 21,269 Minutes	21,269	69404	50,68
2	Peak @ 25,109 Minutes	25,109	67550	49,32

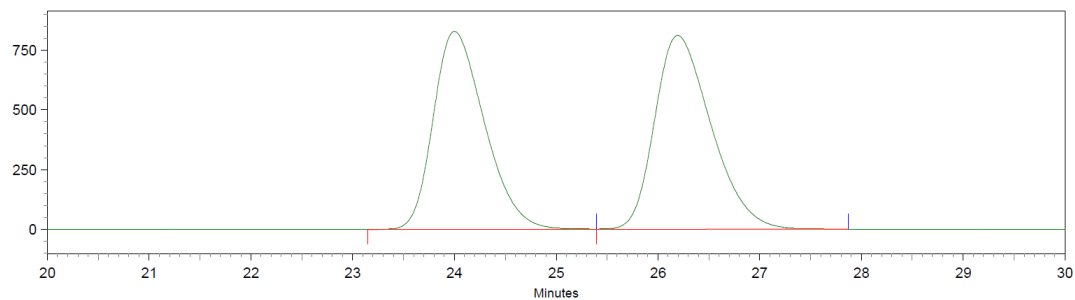
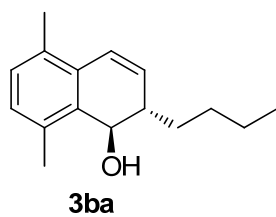
Totals			136954	100,00
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1: 265 nm, 8 nm Results

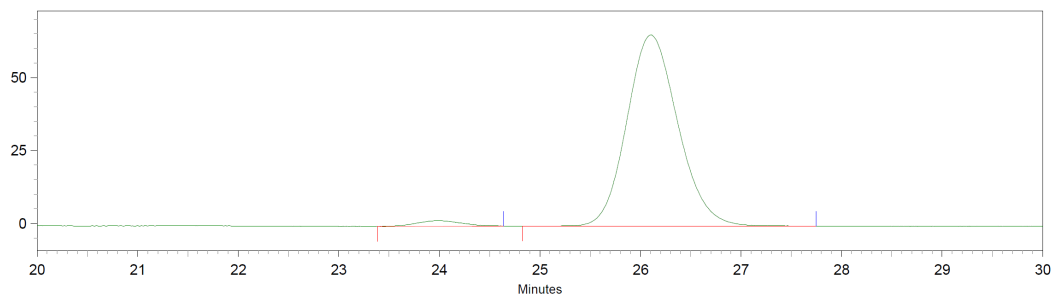
Pk #	Name	Retention Time	Area	Area Percent
1		22,891	40923	1,29
2		26,549	3130817	98,71

Totals			3171740	100,00
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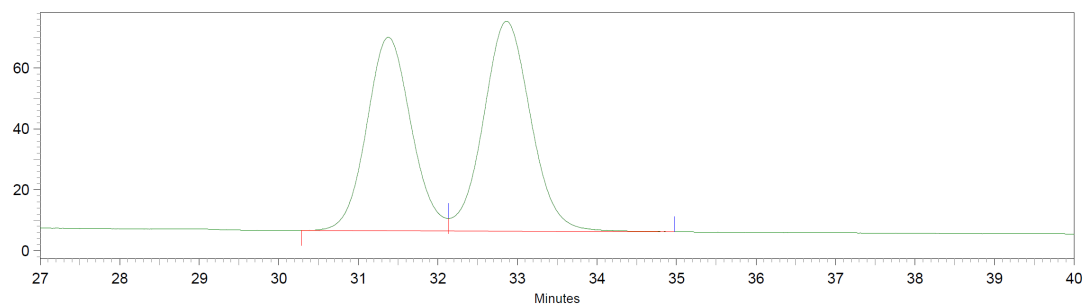
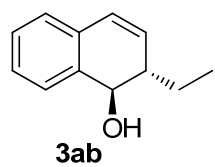
1: 254 nm, 8 nm

Pk #	Name	Retention Time	Area	Area Percent
1	1	24.000	29009088	48.13
2	2	26.197	31258306	51.87
Totals			60267394	100.00



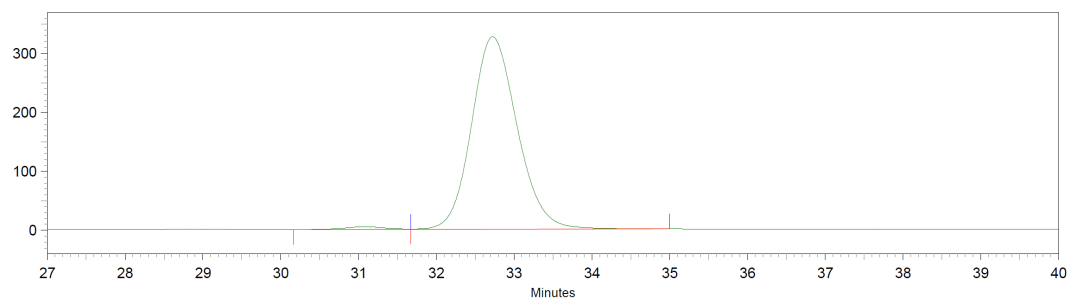
1: 254 nm, 8 nm

Pk #	Name	Retention Time	Area	Area Percent
1	1	23.968	58740	2.48
2	2	26.101	2311439	97.52
Totals			2370179	100.00



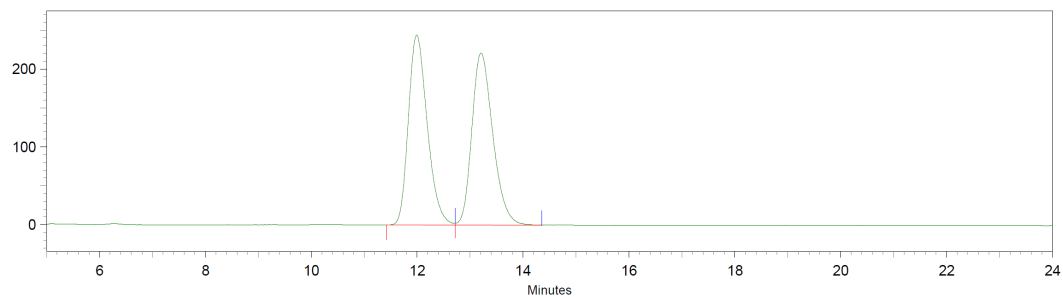
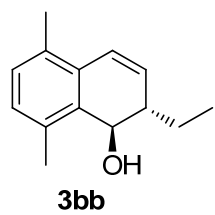
1: 254 nm, 8 nm

Pk #	Name	Retention Time	Area	Area Percent
1	1	31.381	2476813	46.45
2	2	32.864	2855639	53.55
Totals			5332452	100.00



1: 254 nm, 8 nm

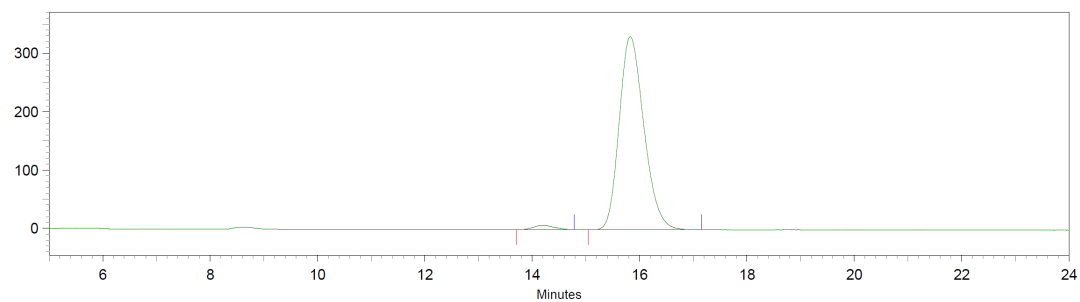
Pk #	Name	Retention Time	Area	Area Percent
1	1	31.072	164506	1.22
2	2	32.725	13329741	98.78
Totals			13494247	100.00



1: 230 nm, 8 nm

Pk #	Name	Retention Time	Area	Area Percent
1	1	11.989	6053272	49.89
2	2	13.205	6081121	50.11

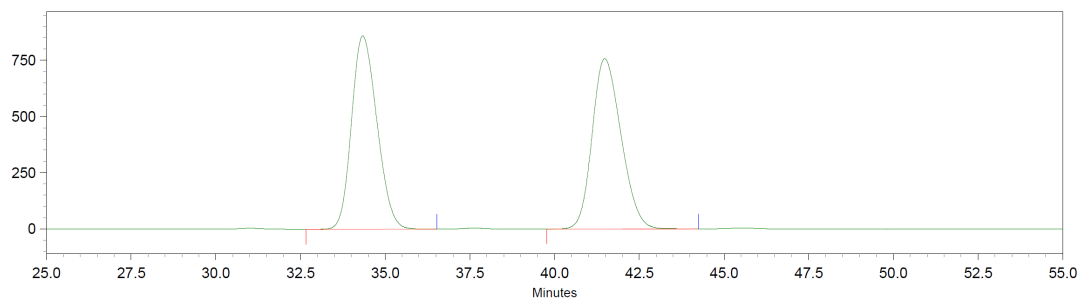
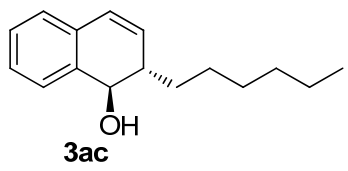
Totals			12134393	100.00
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1: 230 nm, 8 nm

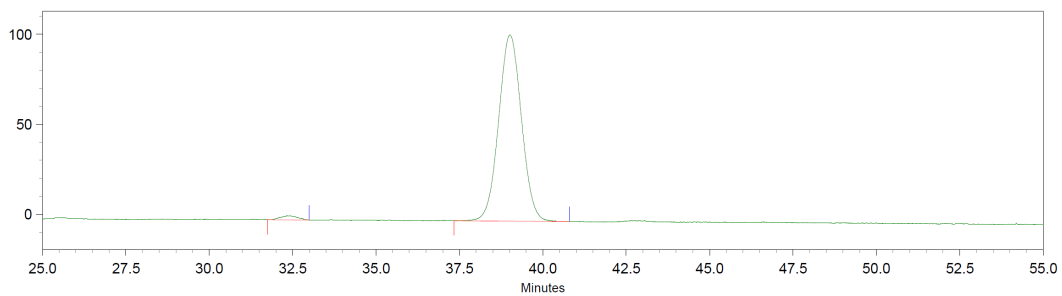
Pk #	Name	Retention Time	Area	Area Percent
1	1	14.208	192293	1.79
2	2	15.829	10565515	98.21

Totals			10757808	100.00
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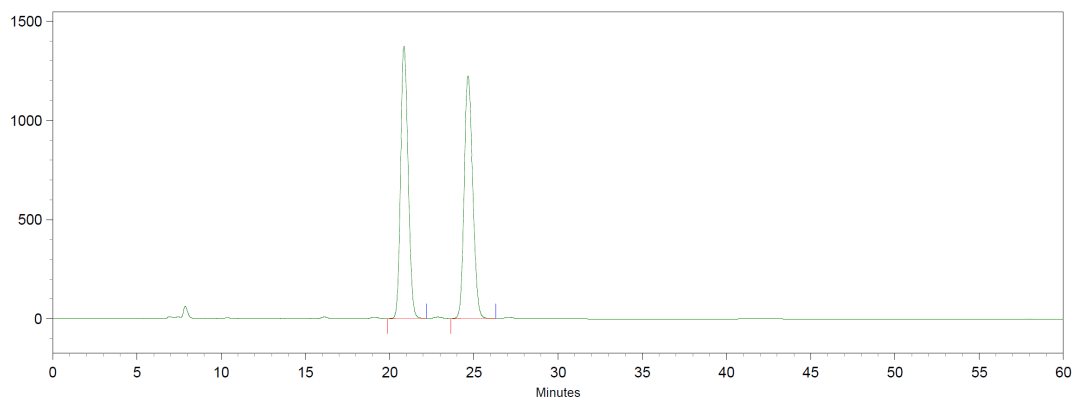
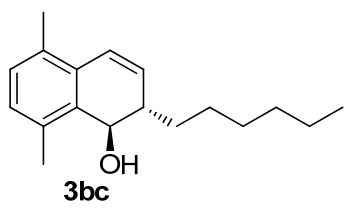
1: 254 nm, 8 nm

Pk #	Name	Retention Time	Area	Area Percent
1	1	34.336	44932466	49.91
2	2	41.483	45092999	50.09
Totals			90025465	100.00



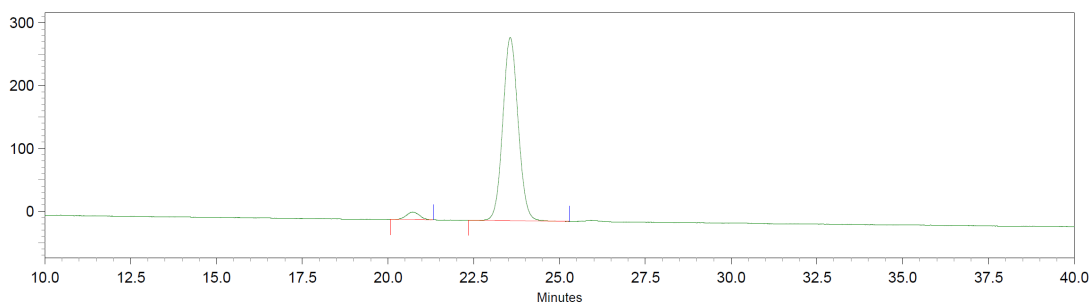
1: 254 nm, 8 nm

Pk #	Name	Retention Time	Area	Area Percent
1	1	32.331	79719	1.59
2	2	39.019	4923771	98.41
Totals			5003490	100.00



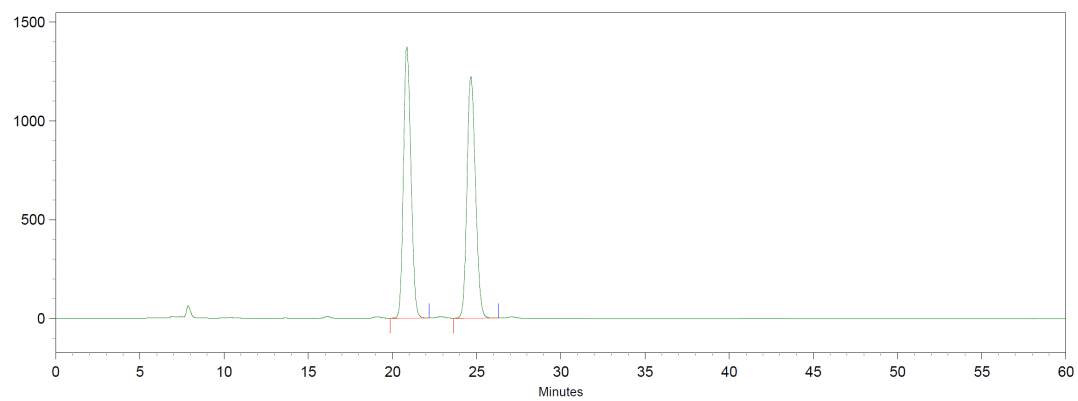
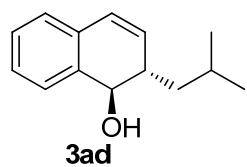
1: 265 nm, 8 nm

Pk #	Name	Retention Time	Area	Area Percent
1	1	20.853	42860165	49.79
2	2	24.661	43217369	50.21
Totals			86077534	100.00



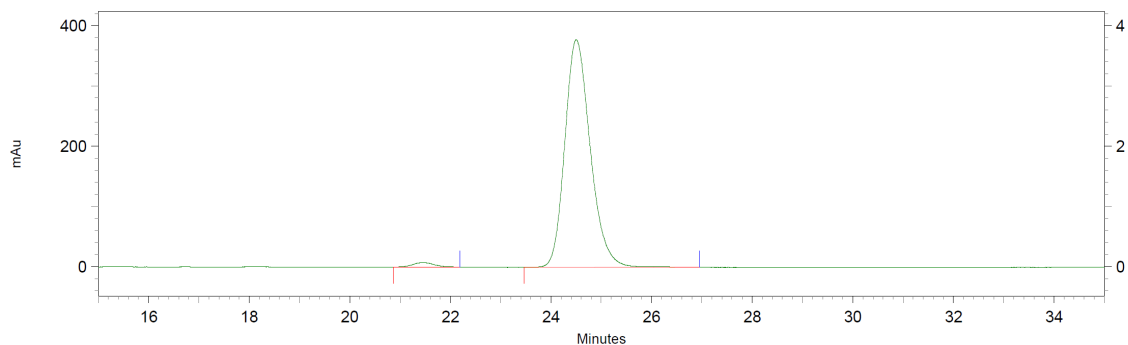
1: 254 nm, 8 nm

Pk #	Name	Retention Time	Area	Area Percent
1	1	20.725	332559	3.53
2	2	23.563	9075925	96.47
Totals			9408484	100.00



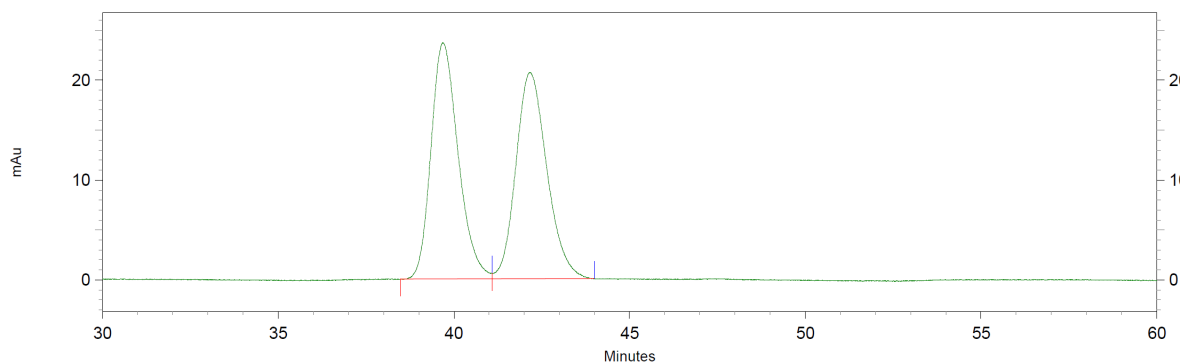
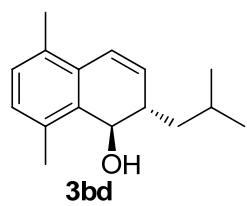
1: 265 nm, 8 nm

Pk #	Name	Retention Time	Area	Area Percent
1	1	20.853	42860165	49.79
2	2	24.661	43217369	50.21
Totals			86077534	100.00



1: 254
nm, 2 nm
Results

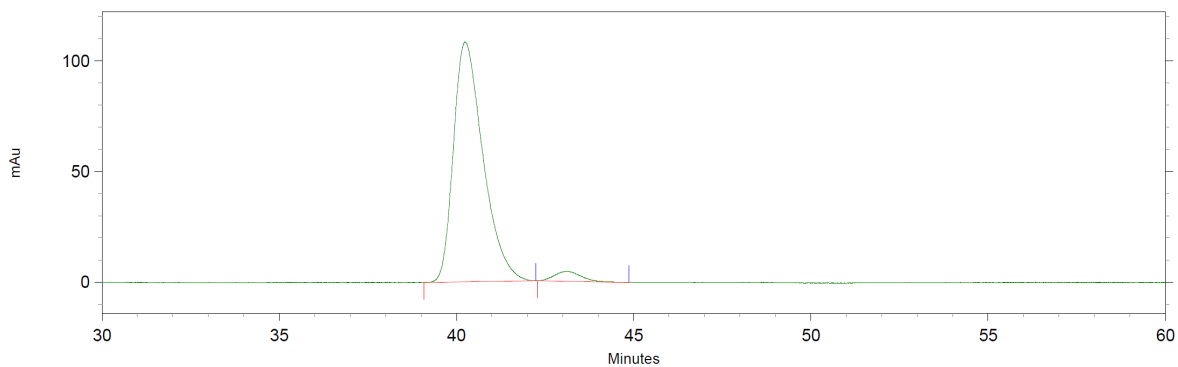
Pk #	Name	Retention Time	Area	Area Percent
1	Peak @ 21,452 Minutes	21,452	231529	1,712
2	Peak @ 24,504 Minutes	24,504	13291143	98,288
Totals			13522672	100,000



1: 254
nm, 2 nm
Results

Pk #	Name	Retention Time	Area	Area Percent
1	Peak @ 39,692 Minutes	39,692	1272363	50,124
2	Peak @ 42,156 Minutes	42,156	1266073	49,876

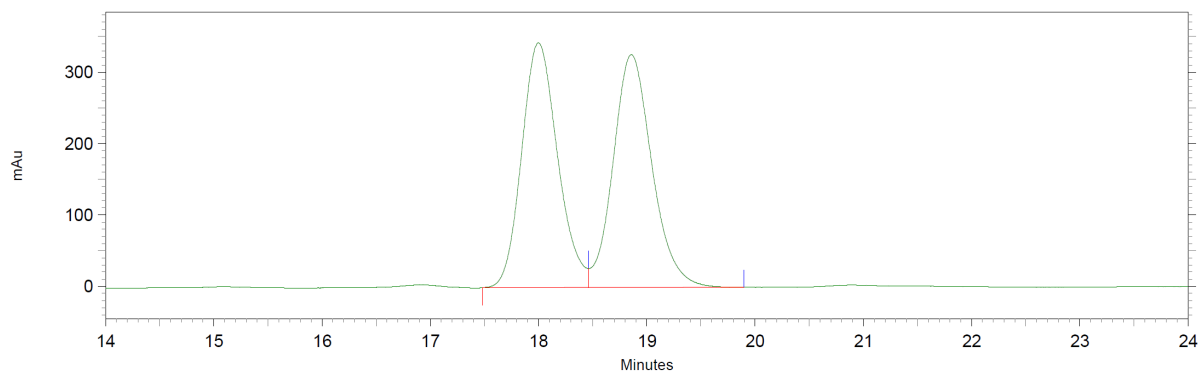
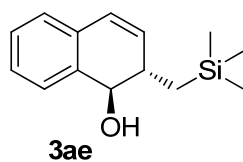
Totals			2538436	100,000
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1: 254
nm, 2 nm
Results

Pk #	Name	Retention Time	Area	Area Percent
1	Peak @ 40,248 Minutes	40,248	6286522	96,378
2	Peak @ 43,108 Minutes	43,108	236262	3,622

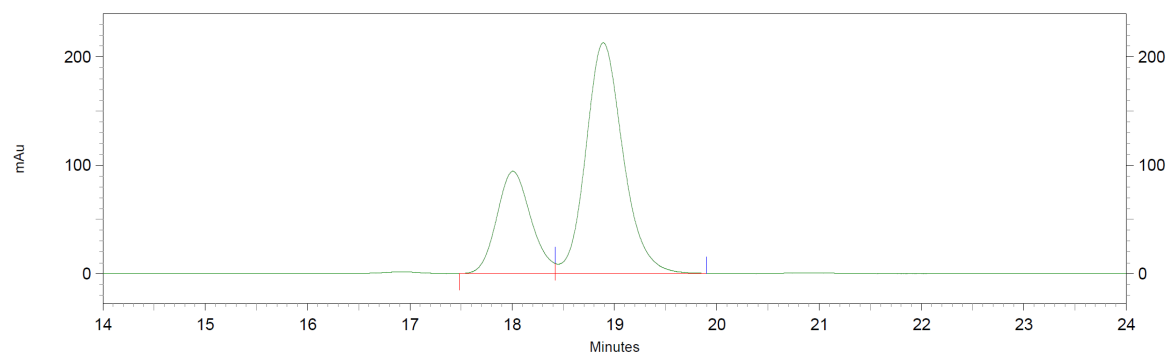
Totals			6522784	100,000
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1: 215 nm,
2 nm Results

Pk #	Name	Retention Time	Area	Area Percent
1	Peak @ 18,008 Minutes	18,000	7932686	49,281
2	Peak @ 18,888 Minutes	18,856	8164275	50,719

Totals			16096961	100,000
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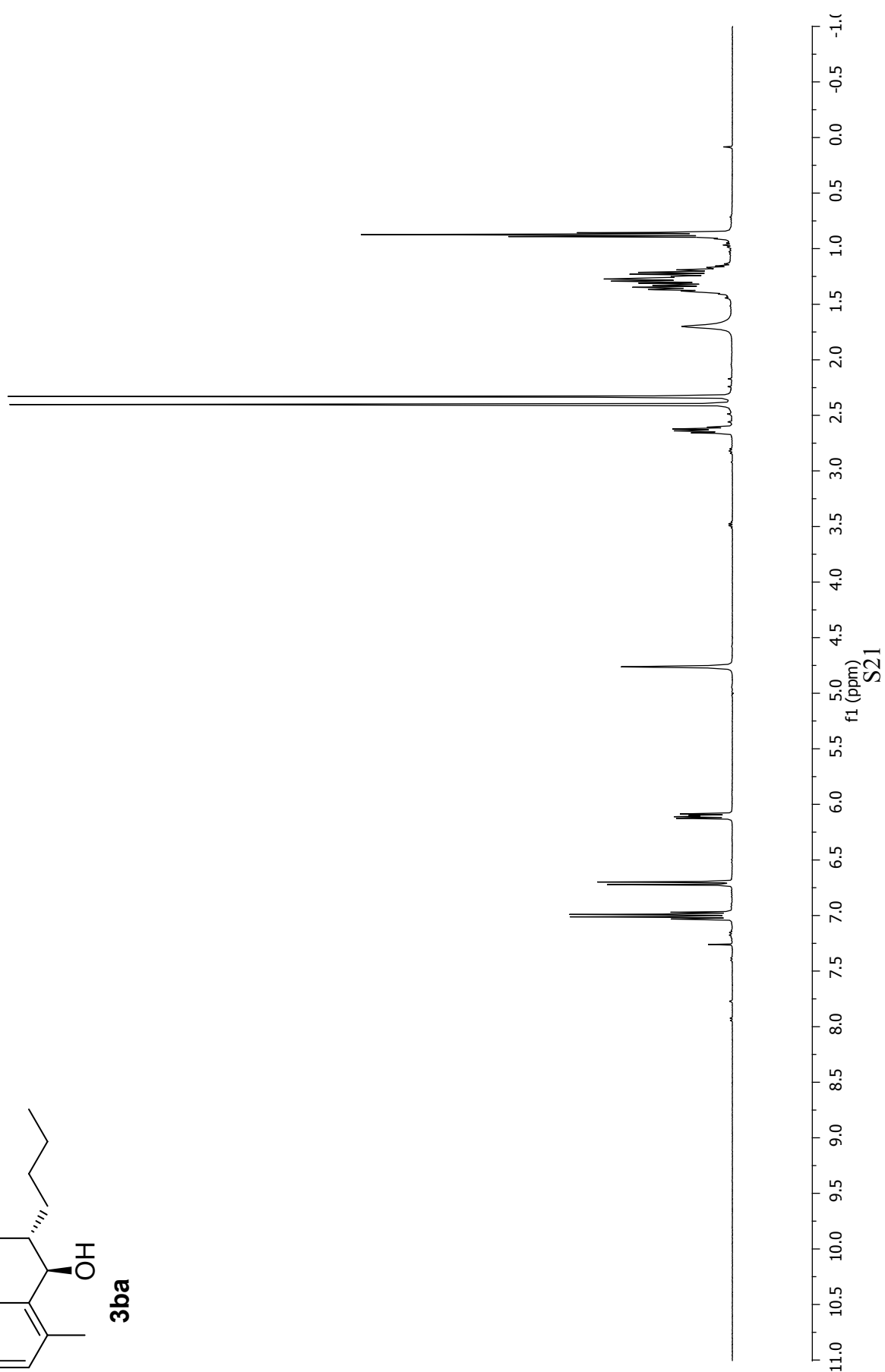


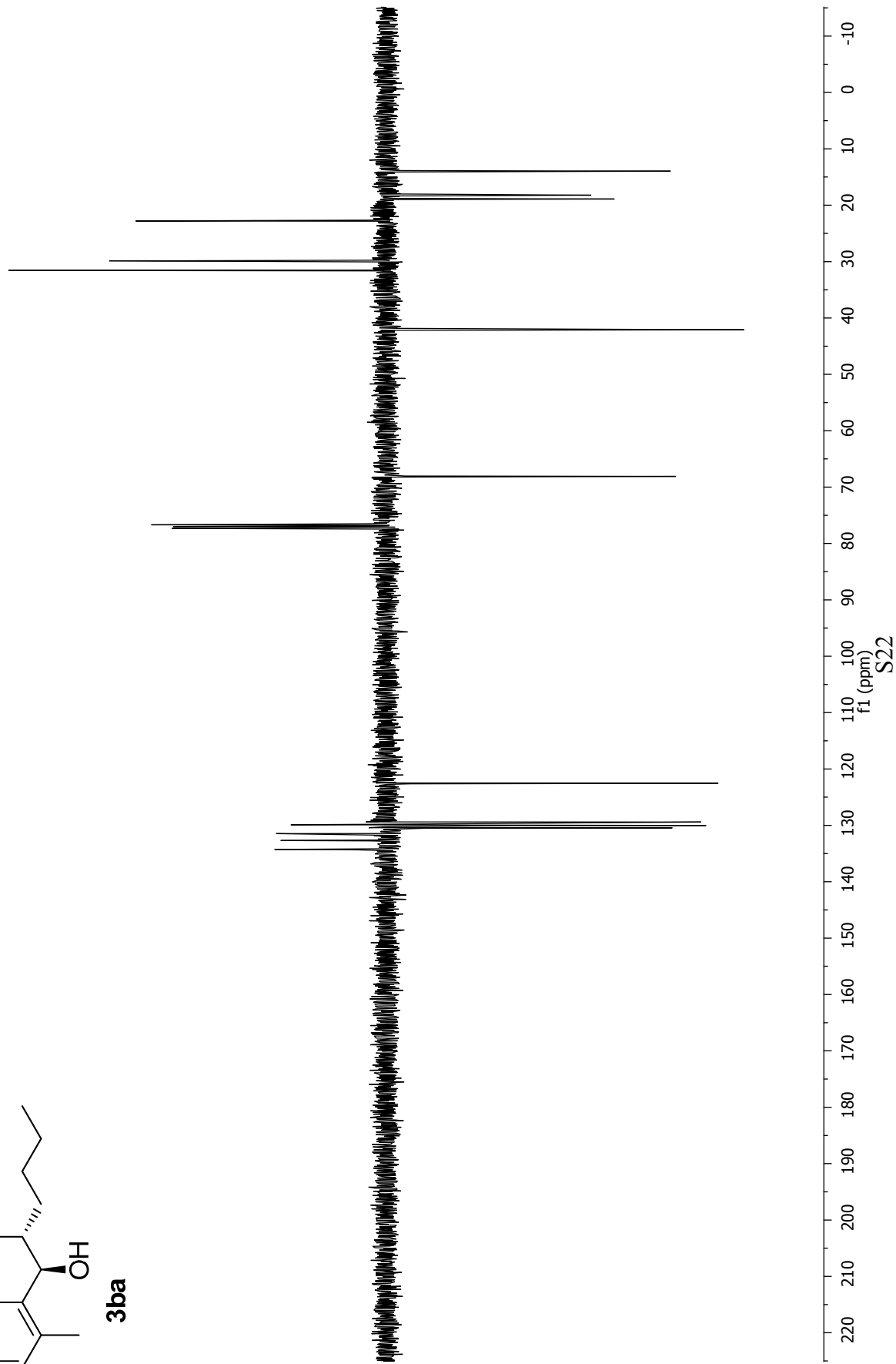
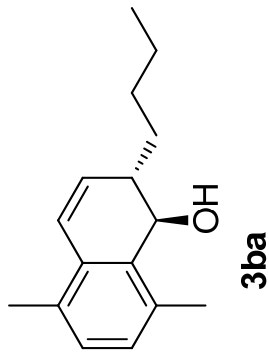
1: 215 nm,
2 nm Results

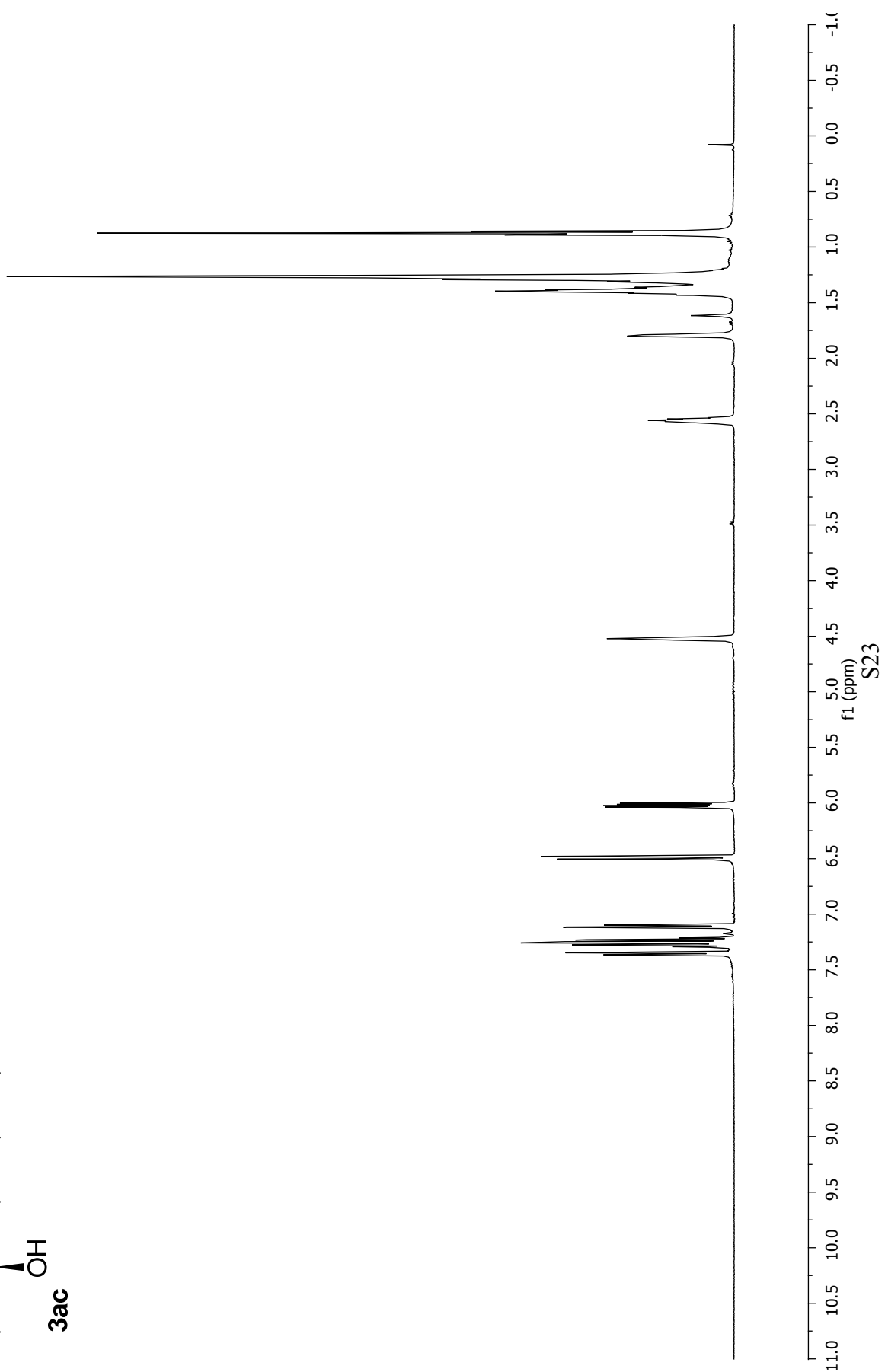
Pk #	Name	Retention Time	Area	Area Percent
1	Peak @ 18,008 Minutes	18,008	2181610	28,852
2	Peak @ 18,888 Minutes	18,888	5379860	71,148

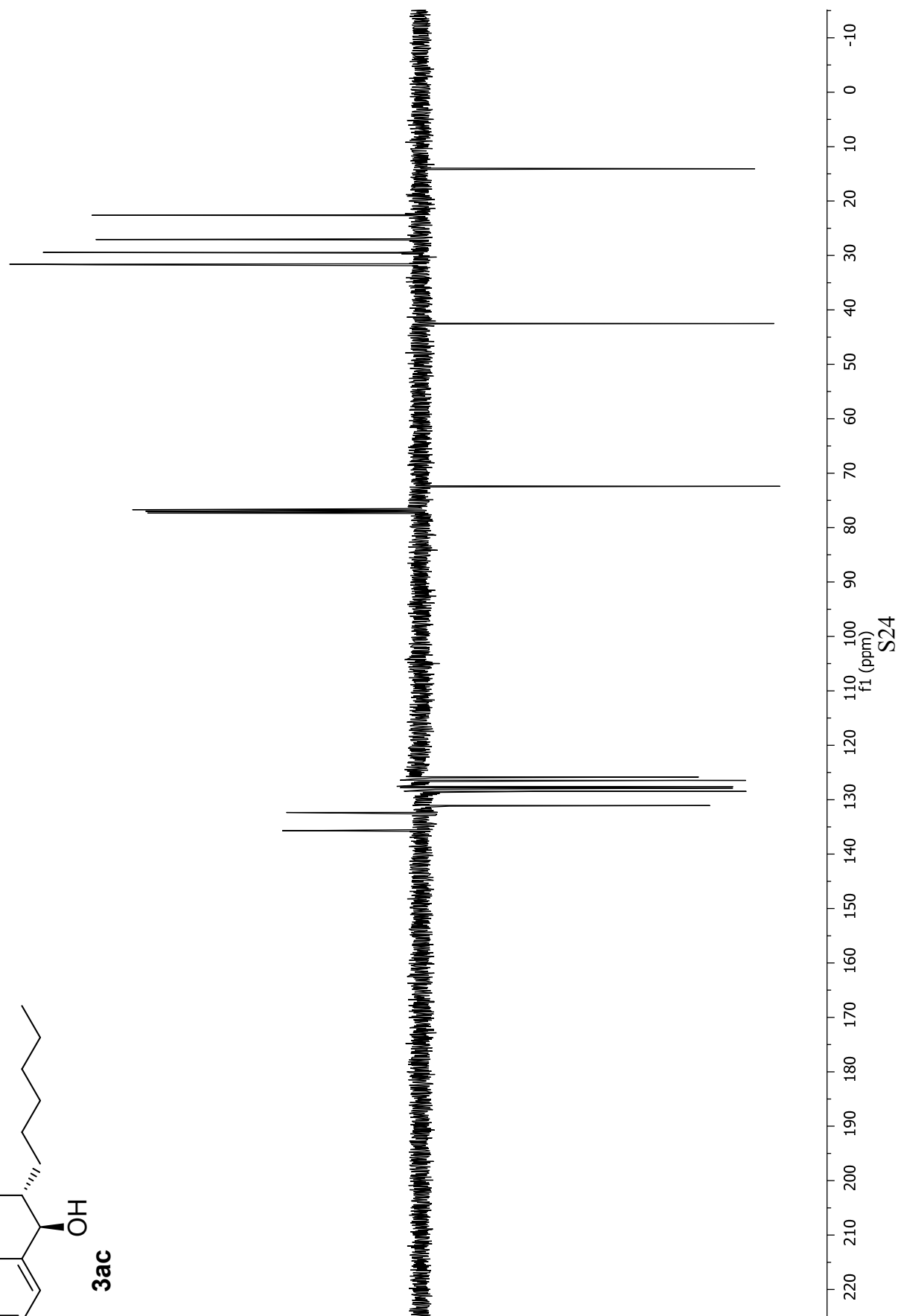
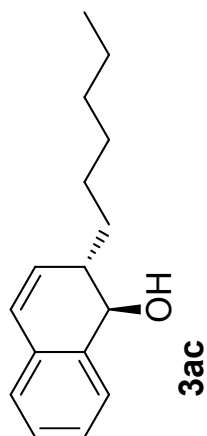
Totals			7561470	100,000
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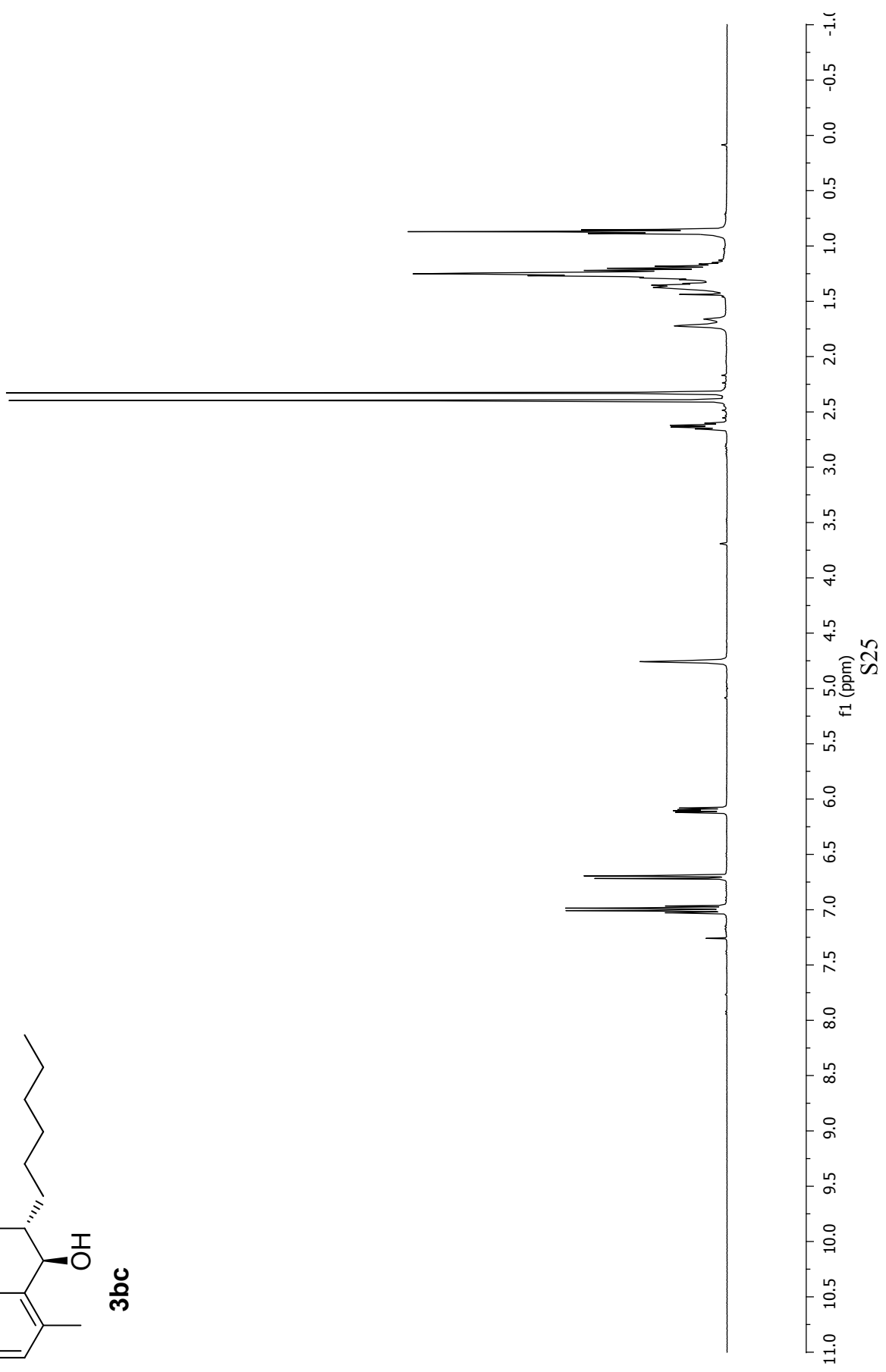
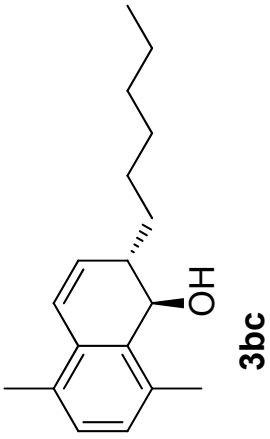
NMR spectra of new compounds

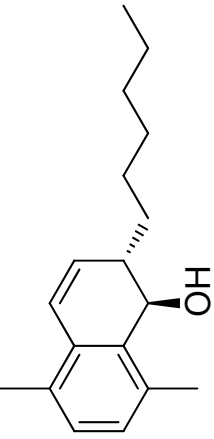












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